Supporting Information

Arenediazonium Salts as Electrophiles for the Oxidative Addition of Gold(I)

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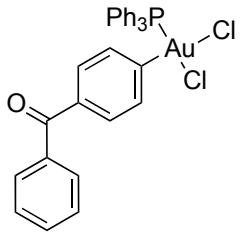
General Information

All reactions were carried out under a nitrogen atmosphere using standard Schlenk tecniques. THF was dried over sodium and freshly distilled prior to use. $CDCl_3$, DMSO-d_6 and commercial reagents were purchased from Aldrich and used as received without further purification. Silver acetylides were synthesized and stored protected from light. Reactions containing silver salts were protected from light in order to prevent its decomposition. Thin layer chromatography was carried out using TLC Alugram G/UV254 0.20 mm. Chromatography purifications were performed using flash grade silica gel (SDS Chromatogel 60 Acc, 40-60 μm). NMR spectra were recorded at 25 ºC on a Jeol Eclipse 300 Mz, Bruker Avance 400 Mz and Varian Unity Inova 500 MHz spectrometers. Chemical shifts are reported in ppm. High resolution mass spectra (HRMS) were recorded and on a Jeol The Accutof JMS-T100LC spectrometer using plolyethylene glycol as internal standard. Melting points were determined using a Reichert microscope apparatus and were uncorrected.

***cis*-(4-Benzoylphenyl)dichlorotriphenylphosfine gold(III) (3b):**

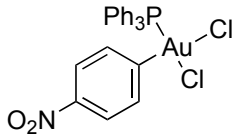


To a solution of 4-aminobenzophenone (10.05 mg, 0.05 mmol) in THF (1.50 mL) was added $HCl{\cdot}OEt_2$ (102.00 μL, 0.10 mmol, 1 M) at 0 ºC. The mixture was stirred until a white precipitate appeared then, was cooled to -15 ºC and *tert*-butyl nitrite (7.30 μL, 0.06 mmol) was added dropwise. The reaction mixture was stirred from -15 ºC to 0 ºC over a period of 20 min, thereafter the solution was removed under vacuum. Next the diazonium salt was dissolved in DMSO (1.50 mL), and $[AuCl(PPh_3)]$[1] (25.00 mg, 0.05 mmol) was added under nitrogen. The temperature was up to 50 ºC and the mixture was heated until total

[1] This complex was synthesized according to: C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc*. **2005**, *127*, 6178-6179.

consumption of the diazonium salt. Later the solvent was removed under vacuum and the residue obtained was redissolved in CH_2Cl_2 and crystalized by slow diffusion of Et_2O. The crystals obtained were washed with Et_2O and dried. Colourless crystals (13.70 mg, 38%), mp = 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.2 Hz, 2H), 7.63-7.36 (m, 18H), 7.22 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.77 (C), 152.81 (C), 137.35 (C), 135.40 (C), 134.78 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH), 133.22 (d, $J_{C\text{-}P}$ = 2.0 Hz, CH), 132.61 (CH), 131.35 (CH), 131.24 (CH), 130.06 (CH), 129.33 (d, $J_{C\text{-}P}$ = 12.5 Hz, CH), 128.40 (CH), 123.77 (d, $J_{C\text{-}P}$ = 68.4 Hz, C). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.70. HRMS-DART calculated for $C_{31}H_{24}AuClOP$ $[M\text{-}Cl]^+$: 675.09188; found: 675.09160.

***cis*-(4-Nitrophenyl)dichlorotriphenylphosfine gold(III) (4):**



This complex was synthesized following the protocol employed for the synthesis of **3b**. Colourless crystals (21.50 mg, 41%), mp = 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.35 (m, 17H), 7.16 (d, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.62 (C), 145.97 (C), 134.70 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH), 133.45 (d, $J_{C\text{-}P}$ = 2.4 Hz, CH), 132.05 (CH), 129.41 (d, $J_{C\text{-}P}$ = 12.6 Hz, CH), 124.10 (CH), 123.37 (d, $J_{C\text{-}P}$ = 68.6 Hz, C). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.93. HRMS-DART calculated for $C_{24}H_{19}AuClNO_2P$ $[M\text{-}Cl]^+$: 616.05074; found: 616.05286.

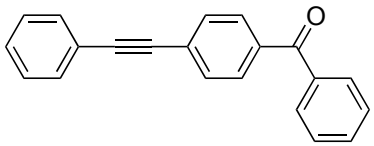
General method for the coupling of anilines with silver acetylides:

To a solution of the corresponding aniline (0.05 mmol) in THF (1.50 mL) was added $HCl{\cdot}OEt_2$ (0.10 mmol, 1 M) at 0 ºC. The mixture was stirred until a white precipitate appeared then, was cooled to -15 ºC and *tert*-butyl nitrite (0.06 mmol) was added dropwise. The reaction mixture was stirred from -15 ºC to 0 ºC over a period of 20 min, thereafter the solution was removed under vacuum. Next, the diazonium salt was dissolved in DMSO (1.50 mL), and $[AuCl(SMe_2)]$[2] (0.05 mmol) was added under nitrogen. The temperature

[2] This complex was synthesized according to: M. Zhang, A. Abdukader, Y. Fu, C. Zhu,

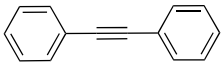
was up to 50 ºC and the mixture was heated until total consumption of the diazonium salt (the reaction time was determined by ^{1}HNMR). Later the reaction mixture was cooled to r.t. and the corresponding silver acetylide was added (0.07 mmol). The reaction was further stirred at r.t. for 1 h, then solvent was removed under vacuum, and product obtained was finally purified by silica gel chromatography using mixtures of hexane/EtOAc as eluent.

4-(Phenylethynyl)benzophenone:[3]



White solid. Obtained: 10.80 mg (75%). ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.80 - 7.77 (m, 4H), 7.67 - 7.54 (m, 5H), 7.53 - 7.46 (m, 2H), 7.40 - 7.35 (m, 3H).^{13}C RMN (400 MHz, $CDCl_3$) δ 196.10 (C), 137.59 (C), 136.90 (C), 132.68 (CH), 131.90 (CH), 131.56 (CH), 130.23 (CH), 130.12 (CH), 128.93 (CH), 128.59 (CH), 128.51 (CH), 127.75 (C), 92.62 (C), 88.81 (C). HRMS-DART calculated for $C_{21}H_{15}O_1$ $[M+H]^+$: 283.11229; found: 283.11203. IR (ATR): ν 1642, 1282, 748, 688, 511 cm^{-1}.

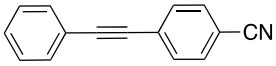
Diphenylacetylene:[4]



Yellowish solid. Obtained: 5.30 mg (19 %). ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 4H), 7.39 – 7.32 (m, 6H). ^{13}C RMN (400 MHz, $CDCl_3$) δ 131.75 (CH), 128.48 (CH), 128.40 (CH), 123. 42 (C), 89.51 (C).

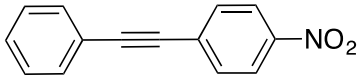
4-(Phenylethynyl)-benzonitrile:[5]

Molecules, **2012**, *17*, 2812-2822.
[3] A. Fürstner, G. Seidel, *Tetrahedron* **1995**, *51*, 11165-11176.
[4] V. Sashuk, J. Ignatowska, K. Grela, *J. Org. Chem*. **2004**, *69*, 7748-7751.
[5] H. Huang, H. Liu, H. Jiang, K. Chen, *J. Org. Chem*. **2008**, *73*, 6037-6040.



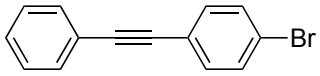
Yellowish solid. Obtained: 9.5 mg (48%) ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 4H), 7.57 – 7.52 (m, 2H), 7.42 – 7.34 (m, 3H). ^{13}C RMN (400 MHz, $CDCl_3$) δ 132.20 (CH), 132.19 (CH) 131.92 (CH), 129.86 (CH), 128.64 (CH), 128.39 (C), 122.35 (C), 118.67 (C), 111.61 (C), 93.92 (C), 87.86 (C). HRMS-DART calculated for $C_{15}H_{10}N_1$ $[M+H]^+$: 204.08132; found: 204.08102. IR (ATR): 2223, 2211, 1600, 1499, 1272, 839, 759, 690, 555, 530 cm^{-1}.

1-Nitro-4-(2-phenylethynyl)benzene:[6]



Yellowish solid. Obtained: 13.8 mg (60%) ^{1}H RMN (400 MHz, $CDCl_3$) δ 8.18 - 8.11 (m, 2H), 7.62 – 7.56 (m, 2H), 7.51 – 7.45 (m, 2H), 7.36 – 7.28 (m, 3H). ^{13}C RMN (400 MHz, $CDCl_3$) δ 147.11 (C), 132.40 (CH), 131.98 (CH), 130.40 (C), 129.41 (CH), 128.67 (CH), 123.77 (CH), 122.23 (C), 94.84 (C), 87.69 (C). HRMS-DART calculated for $C_{14}H_{10}N_1O_2$ $[M+H]^+$: 224.07115; found: 224.07120. IR (ATR): ν 2211, 1508, 1342, 854, 761, 686, 505 cm^{-1}.

1-Bromo-4-(phenylethynyl)benzene:[7]



Yellowish solid. Obtained: 28 mg (70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 - 7.44 (m, 4H), 7.43 – 7.31 (m, 5H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 133.16 (CH), 131.75 (CH), 131.73 (CH), 128.83 (C), 128.65 (CH), 128.54 (CH), 123.04 (C), 122.38 (C), 90.64 (C), 88.44 (C). HRMS-DART calculated for $C_{14}H_{10}Br_1$ $[M+H]^+$: 256.99659; found 256.99711.

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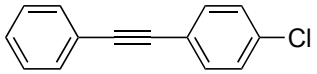
[6] S. B. Park, H. Alper, *Chem. Commun*. **2004**, 1306-1307.
[7] P. Karastatiris, J. A. Mikroyannidis, I. K. Spiliopoulos, Macromolecules **2004**, *37*, 7867-7878.

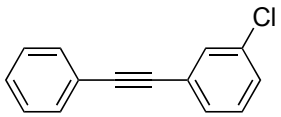
IR (ATR): ν 3051.38, 2659.62, 2915.44, 2845.21, 1601.40, 1492.65, 1389.57, 1074.65, 1004.41, 819.77, 754.07, 504.85 cm^{-1}.

1-Chloro-4-(phenylethynyl)benzene:[8]



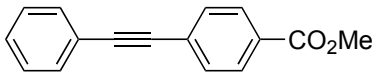
Yellowis solid. Obtained: 19 mg (58%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 - 7.51 (m, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.30 (m, 5H). ^{13}C NMR (300 MHz, $CDCl_3$) δ □134.39 (C), 132.95 (CH), 131.73 (CH), 128.83 (CH), 128.62 (CH), 128.53 (CH), 123.06 (C), 121.91 (C), 90.45 (C), 88.37 (C). HRMS-DART calculated for $C_{14}H_{10}Cl_1$ $[M+H]^+$: 213.04710; found 213.04724. IR (ATR): ν 3045.71, 2915.44, 2845.21, 2221.04, 1916.31, 1585.54, 1492.65, 1091.64, 1015.74, 825.43, 749.54, 510.52 cm^{-1}.

1-Chloro-3-(phenylethynyl)benzene:[9]



Yellowish oil. Obtained: 15 mg (45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 - 7.51 (m, 3H), 7.43 – 7.40 (m, 1H), 7.39 – 7.28 (m, 5H). ^{13}C NMR (300 MHz, $CDCl_3$) δ □134.32 (C), 131.82 (CH), 131.59 (CH), 129.86 (CH), 129.71 (CH), 128.76 (CH), 128.64 (CH), 128.55 (CH), 125.16 (C), 122.9 (C), 90.68 (C), 88.06 (C). HRMS-DART calculated for $C_{14}H_{10}Cl_1$ $[M+H]^+$: 213.04710; found 213.04687. IR (ATR): ν 3057.04, 2926.77, 2845.21, 2226.7, 1579.87, 1492.65, 874.14, 749.54, 537.7 cm^{-1}.

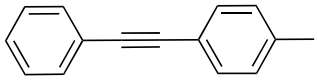
Methyl-4-(phenylethynyl)benzoate:[10]



[8] L. Melzig, A. Metzger, P. Knochel, *Chem. Eur. J.* **2011**, *17*, 2948-2956.
[9] J. Moon, M. Jang, S. Lee, *J. Org. Chem*. **2009**, *74*, 1403-1406.
[10] M. Wu, J. Mao, J. Guo, S. Ji, *Eur. J. Org. Chem*. **2008**, 4050-4054.

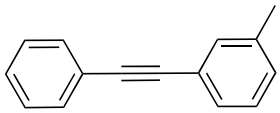
Yellowish oil. Obtained: 8 mg (32%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 - 7.91 (m, 2H), 7.5 – 7.47 (m, 2H), 7.45 – 7.43 (m, 2H), 7.28 – 7.25 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 166.71 (C=O), 131.87 (CH), 131.64 (CH), 129.66 (CH), 129.63 (C), 128.89 (CH), 128.57 (CH), 128.16 (C), 122.86 (C), 92.5 (C), 88.77 (C), 52.37 (CH_3). HRMS-DART calculated for $C_{16}H_{13}O_2$ $[M+H]^+$: 237.09155; found 237.09194. IR (ATR): ν 2921, 2850, 2215, 1710, 1406, 1276, 1101, 852, 759, 695, 516 cm^{-1}.

1-Methyl-4-(2-phenylethynyl)benzene:[11]



Yellowish oil. Obtained: 3.5 mg (35%). ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.44 – 7.42 (m, 2H), 7.35 – 7.31 (m, 3H), 7.17 – 7.15 (m, 2H), 2.37 (s, 3H). ^{13}C RMN (400 MHz, $CDCl_3$) δ 138.53 (C), 131.69 (CH), 131.64 (CH), 129.26 (CH), 128.45 (CH), 128.21 (CH), 123.63 (C), 120.34 (C), 89.70 (C), 88.86 (C), 21.66 (CH_3). HRMS-DART calculated for $C_{15}H_{12}$ $[M]^+$: 192.09390; found: 192.09373. IR (ATR): ν 2213, 1439, 1016, 815, 751, 686, 513 cm^{-1}.

1-Methyl-3-(2-phenylethynyl)-benzene:[12]

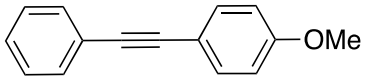


Yellowish oil. Obtained: 5.00 mg (51%). 5 mg (51 %) ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.38 – 7.31 (m, 5H), 7.23 (d, *J* = 7.6 Hz, 1H), – 7.15 (d, *J* = 7.1 Hz, 1H), 2.36 (s, 3H). ^{13}C RMN (400 MHz, $CDCl_3$) δ 138.17 (C), 132.33 (CH), 131. 74 (CH), 129.30 (CH), 128.82 (CH), 128.47 (CH), 128.38 (CH), 128.31 (CH), 123.35 (C), 123.04 (C), 89.53 (C), 89.00 (C), 21.24 (CH_3). HRMS-DART calculated for $C_{15}H_{13}$ $[M+H]^+$:

[11] N. Kakusawa, K. Yamaguchi, J. Kurita, *J. Organomet. Chem*. **2005**, *690*, 2956-2966.
[12] T. Suzuka, Y. Okada, K. Ooshiro, Y. Uozumi, *Tetrahedron* **2010**, *66*, 1064-1069.

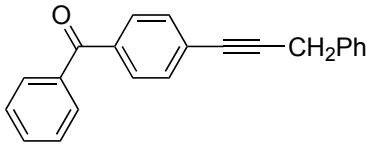
193.10173; found: 193.10160. IR (film): ν 3081, 3039, 2924, 2380, 1601, 1579, 1494, 1443, 1381, 1091, 1070, 1041, 916, 883 cm^{-1}.

1-Methoxy-4-(2-phenylethynyl)-benzene:[13]



Yellowish oil. Obtained: 10.8 mg (75%). ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.29 – 7.22 (m, 3H), 6.85 – 6.77 (m, 2H), 3.76 (s, 3H). ^{13}C RMN (400 MHz, $CDCl_3$) δ 159.75 (C), 133.19 (CH), 131.59 (CH), 128.45 (CH), 128.07 (CH), 123.74 (C), 115.53 (C), 114.14 (CH), 89.50 (C), 88.21 (C), 55.46 (CH_3). HRMS-DART calculated for $C_{15}H_{13}O_1$ $[M+H]^+$: 209.09664; found: 209.09653. IR (ATR): ν 2919, 2215, 1730, 1593, 1507, 1243, 1027, 831, 752, 690, 520 cm^{-1}.

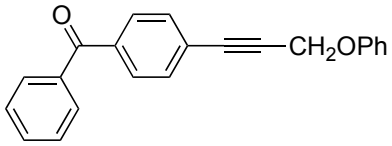
Phenyl[4-(3-phenylprop-1-yn-1-yl)phenyl]nethanone:



Yellowish oil. Obtained: 14.00 mg (47%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 - 7.73 (m, 4H), 7.62 – 7.27 (m, 10H), 3.88 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 196.17 (C=O), 137.61 (C), 136.59 (C), 136.41 (C), 132.63 (CH), 131.63 (CH), 130.16 (CH), 130.10 (CH), 128.79 (CH), 128.48 (CH), 128.19 (C), 128.11 (CH), 126.95 (CH), 91.23 (C), 82.21 (C), 26.01 (CH_2). IR (film): ν 3057, 2981, 2823, 2687, 2410, 2302, 1547, 1428, 1156, 895 cm^{-1}. HRMS-DART calculated for $C_{22}H_{17}O_1$ $[M+H]^+$: 297.12794; found: 297.12798.

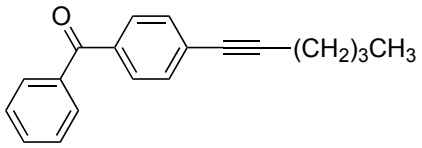
[4-(3-Phenoxyprop-1-yn-1-yl)pheny](phenyl)methanone:

[13] S. B. Park, H. Alper, *Chem. Commun*. **2004**, 1306-1307.



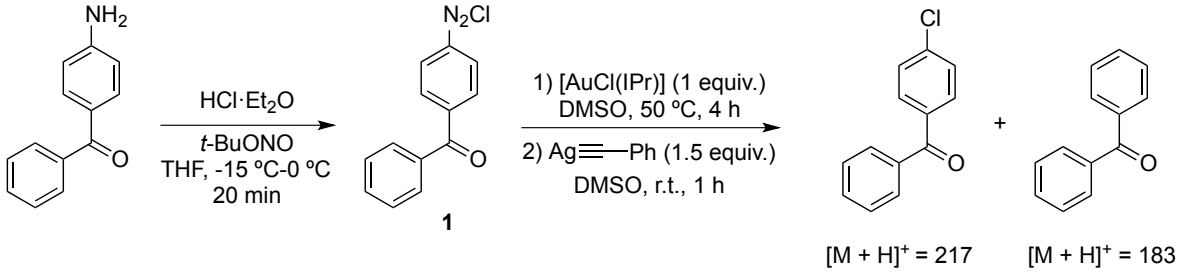
Yellowish oil. Obtained: 14.00 mg (43% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.74 (m, 4H), 7.61 – 7.57 (m, 1H) 7.56 – 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.36 – 7.9 (m, 2H), 7.06 – 6.99 (m, 3H), 4.95 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ □196.023 (C=O), 157.84 (C), 137.41 (C), 137.37 (C), 132.75 (CH), 131.77 (CH), 130.1 (CH), 129.66 (CH), 128.51 (CH), 126.6 (C), 121.73 (CH), 115.10 (CH), 87.15 (C), 86.47 (C), 56.66 (CH_2). IR (film): ν 2981, 2685, 1601, 1595, 1422, 1161, 1150, 895 cm^{-1}. HRMS-DART calculated for $C_{22}H_{17}O_2$ $[M+H]^+$: 313.12285; found: 313.12246.

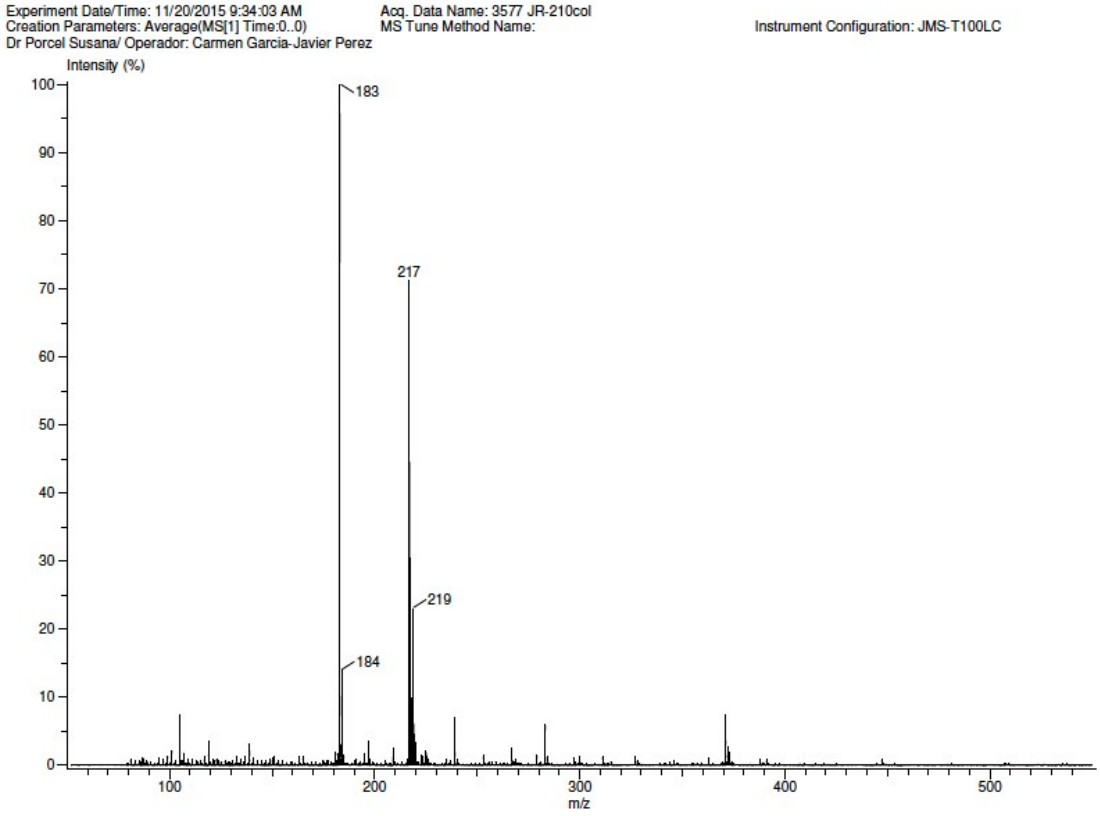
[4-(hex-1-yn-1-yl)phenyl](phenyl)methanone:



Yellowish oil. Obtained: 11.00 mg (26%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.75 (m, 2H), 7.75 - 7.71 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.45 (m, 4H), 2.47 – 2.43 (t, *J* = 7.0 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.54 – 1.45 (m, 2H), 0.98 – 9.94 (t, *J* = 7.3 Hz 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ □196.21 (C=O), 137.69 (C), 136.23 (C), 132.55 (CH), 131.5 (CH), 130.12 (CH), 130.08 (CH), 128.71 (C), 128.44 (CH), 94.26 (C), 80.25 (C), 30.83 (CH_2), 22.17 (CH_2), 19.37 (CH_2), 13.77 (CH_3). IR (film): ν 3057.04, 2986.81, 2687.75, 2514.43, 2415.88, 2302.6, 2252.75, 1655.77, 1428.08, 1264.96, 1156.21, 901.33, 738.21 cm^{-1}. HRMS-DART calculated for $C_{19}H_{19}O_1$ $[M+H]^+$: 263.14359; found: 263.14412.

Analysis by mass spectrometry of the products obtained in the coupling of 1 with silver phenylacetylide mediated by [AuCl(IPr)]

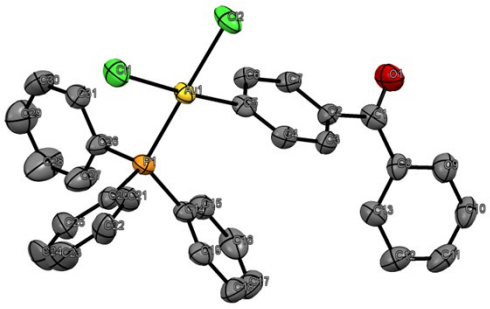




Chyrtallographic data of structures 3b and 4.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1442893 (**3b**), and CCDC-1442894 (**4**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).

ORTEP diagram of 3b

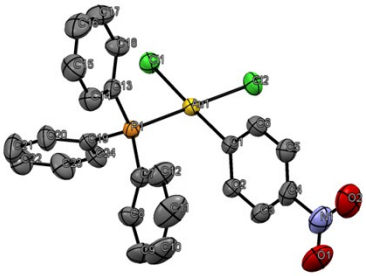


Selected crystal data

Empirical formula	C31 H24 Au Cl2 O P
Formula weight	711.34
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorombic
Space group	P b c a
Unit cell dimensions	a = 13.4335(2) Å, b = 9.7044(2) Å, c = 42.1106(7) Å, α= 90°, β= 90°, γ= 90°
Volume	5489.71(17) Å3
Z	8
Density (calculated)	1.721 Mg/m3
Absorption coefficient	5.635 mm-1
F(000)	2768
Crystal size/color/shape	0.259 x 0.242 x 0.032 mm3/ colourless/lamina
Theta range for data collection	2.458 to 27.103°.
Index ranges	$-17 \le h \le 17$, $-7 \le k \le 12$, $-53 \le l \le 38$
Reflections collected	30849
Independent reflections	6054 [R(int) = 0.1142]

Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	6054 / 0 / 325
Goodness-of-fit on F2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0451, wR2 = 0.0740
R indices (all data)	R1 = 0.0956, wR2 = 0.0931
Largest diff. peak and hole	1.283 and -1.298 e.Å-3

ORTEP diagram of 4



Empirical formula	C24 H19 Au Cl2 N O2 P
Formula weight	652.24
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P\ 2_1/n$
Unit cell dimensions	a = 9.360(3) Å, b = 16.371(5) Å, c = 16.662(5) Å, α= 90°, β= 90°, γ= 90°
Volume	2540.9(14) Å3
Z	4
Density (calculated)	1.705 Mg/m3
Absorption coefficient	6.083 mm-1
F(000)	1256
Crystal size/color/shape	0.367 x 0.162 x 0.128 mm3/ colourless/prism
Theta range for data collection	2.704 to 27.103°.
Index ranges	$-11 \le h \le 11, -20 \le k \le 20, -21 \le l \le 21$
Reflections collected	36347
Independent reflections	5575 [R(int) = 0.0645]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2

Data / restraints / parameters	5575 / 0 / 280
Goodness-of-fit on F2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0602
R indices (all data)	R1 = 0.0473, wR2 = 0.0678
Largest diff. peak and hole	0.589 and -0.480 e.Å-3